STABLE AQUEOUS DISPERSIONS OF NON-IONIC BLOCKED POLYISOCYANATES.

DESCRIPTION.

The present invention relates to a process for the preparation of stable aqueous dispersions of non-ionic blocked polyisocyanates and to the dispersions obtained thereby. The aqueous dispersions of the invention are especially useful in combination with organic perfluorinated polymeric compounds in the oil- and/or water-repellent finishing of textiles, as they provide an excellent fixing of the organic perfluorinated polymers on textiles and high washing stability of the treatment.

The proce ss of the invention provides aqueous dispersions of non-ionic blocked polyisocyanates that, unlike the analogous ionic compounds, possess a good compatibility with other adjuvants normally used in textile finishing, independently from their ionicity.

Moreover, the aqueous dispersions of the invention are useful as cross-linkers for textile printing pastes.

One of the problem often encountered in the formulation of aqueous dispersions of non-ionic blocked polyisocyanates is their poor stability.

The process according to the invention allows the obtainment of highly stable aqueous dispersions of non-ionic blocked polyisocyanates.

In the present text with the expression "stable dispersions" we mean dispersions having average particle diameters lower than 1000 nm and that do not show sedimentation after seven days at room temperature.

DESCRIPTION OF THE PRIOR ART

The use of aqueous dispersions of blocked polyisocyanates in textile, paint and coating industry is well known.

In the textile industry, and especially in the finishing of textiles, these dispersions are usually co-formulated with other products, mainly with fluorocarbon emulsions and/or dispersions and applied onto the article by thermal treatment.

During the heating step, the blocked polyisocyanate dissociates so that the isocyanate groups become available to react with the active hydrogen

atoms that are contained in the fibrous material and/or in the perfluorinated polymer.

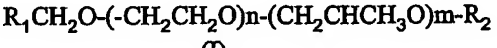
As reported in WO 9952961, the dispersions of ionically stabilised blocked polyisocyanates have the disadvantage that they are not necessarily compatible with other products of opposite ionicity that are generally used in the finishing of textiles, and therefore they can not be applied in combination with them.

To overcome this problem, WO 9952961 describes the use and production of non-ionic blocked polyisocyanates that unfortunately have the disadvantage to be unstable after being dispersed in water and cannot be easily used in industrial application.

US 5,693,737 describes the simultaneous presence of an ionic group (given by a sulfonate diol) and of an alkoxylated monofunctional long chain alcohol to stabilise the aqueous dispersions of blocked polyisocyanates; unfortunately the sulfonate diols used in US 5,693,737 are not easily available on the market and their synthesis is not simple.

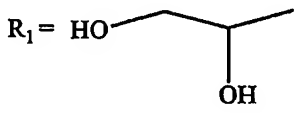
DETAILED DESCRIPTION

It has now surprisingly been found that the aqueous dispersions of non-ionic blocked polyisocyanates obtained from the reaction of a polyisocyanate, a blocking agent and an non-ionic alkoxylated diol having general formula I:



(I)

wherein:



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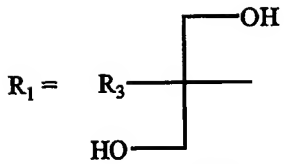


(III)

R_2 and R_3 are equal or different and are chosen among methyl, ethyl, n-propyl, i-propyl, n-butyl, I-butyl;

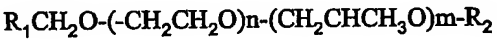
n is a number from 0 to 40;

m is a number from 0 to 40;

n + m is a number from 20 to 80, preferably from 20 to 40,

are stable and particularly suited for the use in the textile field.

The preferred non-ionic alkoxylated diols of the invention have the general formula I:



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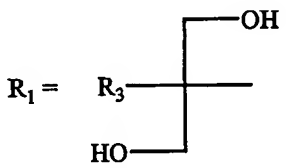


(III)

R_2 is methyl, R_3 is ethyl, n is a number from 15 to 30 and m is a number from 0 to 10; examples of said diols are the commercially available Tegomer ® D-3403 and Tegomer ® D-3123 from Th. Goldschmidt AG (DE).

The stability of the aqueous dispersions of the present invention is the more unexpected as the use of the analogue mono-functional alcohols, instead of the non-ionic alkoxylated diols, leads to the obtainment of unstable dispersions that are not suited for the industrial use.

The polyisocyanates utilisable according to the present invention are those commercially available and containing from 2 to 10 isocyanate groups per

molecule and may be either of the aromatic, or the aliphatic, or the cycloaliphatic or the mixed type.

Examples of suitable polyisocyanates include:

A) diisocyanates, such as 1,6-hexamethylenediisocyanate, 1-isocyanate-3-isocyanate-methyl-3,5,5-trimethyl-cyclohexane (or isophoronediisocyanate), 4,4'-dicyclohexyl-methanediisocyanate, 2,4-toluenediisocyanate either alone or in admixture with 2,6-toluenediisocyanate, 4,4'-diphenyl-methanediisocyanate, meta-tetramethylxilylenediisocyanate or mixtures thereof;

B) tri- and higher-functionalised polyisocyanates, such as the compounds obtained by condensation of trimethylol propane or other polyols having functionality higher than three, and the diisocyanates of point A);

C) compounds obtained by trimerisation, biuretisation, urethanisation or allophanation of the polyisocyanates of the points A) and B), containing at least three isocyanate groups per molecule.

For the realisation of the present invention the preferred polyisocyanates are the isocyanurate obtained from 1,6-hexamethylenediisocyanate and the reaction product of trimethylol propane and toluenediisocyanate (its isomers 2,4 and 2,6 being in a weight ratio of 80:20).

The blocking agents useful for the realisation of the invention are the normally used blocking agents of the reversible kind, thermally de-blockable, such as the compounds containing active methylenic groups (such as the derivatives of malonic acid and its esters, acetylacetone, acetoacetic acid and its esters); oximes; ε-caprolactames and lactames; pyrazoles; imidazoles.

The preferred blocking agents are the ones de-blockable at a temperature of 90°-160°C.

Particularly useful for the realisation of the present invention are oximes and pyrazoles, and more specifically butanone oxime and 3,5-dimethylpyrazole.

According to a fundamental aspect of the invention the process for the preparation of the aqueous dispersions of non-ionic blocked polyisocyanates comprises the following steps:

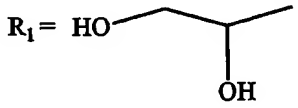
5

a. a polyisocyanate and a non-ionic alkoxylated diol of the general formula

$$R_1CH_2O\text{-}(\text{-}CH_2CH_2O)n\text{-}(CH_2CHCH_3O)m\text{-}R_2$$

(I)

wherein



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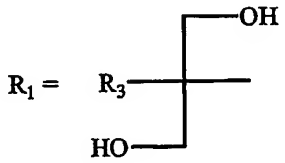

(III)

R_2 and R_3 are equal or different and are chosen among methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl;
n is a number from 0 to 40;
m is a number from 0 to 40;
n + m is a number from 20 to 80, preferably from 20 to 40
are reacted at a temperature of 0°-120°C, their equivalent ratio being such that the percentage of free isocyanate groups in the resulting oligomer is from 3 to 10 and the percentage in weight of ethoxyl groups is from 10 to 40%, preferably from 20 to 30%;

b. the thus obtained oligomer is reacted with an amount of blocking agent such that the equivalent ratio of the isocyanate groups of the oligomer

and the blocking agent is from 1:0.98 to 1:1.30, preferably from 1:1 to 1:1,20;

c. the thus obtained mixture is dispersed into water under vigorous stirring to obtain a dispersion having a solid content of from 20 to 40% by weight, preferably from 25 to 35% by weight.

Advantageously, step b. of the process according to the invention may be preceded by dilution of the reaction mixture obtained in a. with from 0.10 to 0.50 parts by weight of a water mixable polar solvent, said solvent being removed by distillation after completing of step c.; the preferred water mixable polar solvents are aliphatic ketones, such as methyl ethyl ketone, acetone, cyclohexanone.

The process of the invention allows the direct preparation of non-ionic blocked polyisocyanates which are stable for at least six months at ambient temperature, without the need of emulsifiers, surfactants or external dispersants.

The dispersions obtained according to the process of the invention can advantageously be used in the preparation of textile finishing aids, and particularly in the preparation of compositions for the oil- and/or water-repellent finishing of textiles containing organic perfluorinated polymeric compounds.

Said polymeric compounds are those normally used for these applications; among them we cite:

1) homopolymers of acrylic monomers having general formula:

$C_nF_{2n+1}CH_2CH_2OC(O)\text{-}C(R)=CH_2$

wherein:

R is methyl or hydrogen and n is a number from 5 to 12;

2) homopolymers of acrylic monomers having general formula:

$C_nF_{2n+1}SO_2N(R')CH_2CH_2OC(O)\text{-}C(R)=CH_2$

wherein:

R and R' are an alkyl group or hydrogen and n is a number from 5 to 12.

3) copolymers of the above cited fluorinated acrylic monomers with: butadiene, isoprene, chloroprene, styrene, α-methylstyrene, p-methylstyrene, vinyl halides (such as vinyl chloride, vinylidene chloride,

vinylidene fluoride), vinyl esters (such as vinyl acetate, vinyl propionate, vinyl stearate), vinyl methyl ketones, esters or acrylic or methacrylic acid (such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, butyl acrylate, 2-ethylhexyl acrylate or methacrylate, decyl acrylate, lauryl acrylate or methacrylate, stearyl methacrylate, N,N-dimethylaminoethyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate or glycidyl methacrylate), acrylamide, methacrylamide, N-methylol acrylamide, acrylonitrile, methacrylonitrile, N-substituted maleic imides, acrylates or methacrylates of ethoxylated alcohols having molecular weight smaller than 2000 daltons or mixture thereof.

For the preparation of the compositions useful for the oil- and/or water-repellent finishing of textiles, the dispersions of the invention are normally used in an amount of from 0.1 to 10% by weight on the total weight of the composition.

Advantageously the weight ratio between the solid fraction of the dispersion of the invention and the perfluorinated polymeric organic compounds of the oil- and/or water-repellent compositions is comprised between 1:1 and 1:15, more preferably between 1:2 and 1:7.

The finishing step can be performed by using the conventional techniques, for example by impregnation or spray technique, at a temperature of from 80° to 110°C followed by heat treatment at 130°-200°C for 0.5 –6 minutes.

The compositions for the oil- and/or water-repellent finishing of texiles containing the aqueous dispersions of the invention are stable and the textiles treated therewith exhibit high washing stability of the finishing.

The aqueous dispersions of the invention are moreover particularly useful as cross-linkers for textile printing pastes.

The textiles printed with the printing pastes including the aqueous dispersions of the invention as cross-linkers show high colour and washing fastness.

For the preparation of the printing pastes, the aqueous dispersion of the invention are used in an amount of from 0.3 to 5% by weight, preferably of from 1 to 3.5% by weight, on the total weight of the paste.

The examples that follow are presented to better illustrate the invention.

In the examples the following compounds are used:

Polyether 1 = Tegomer ® D-3403, ethoxylated diol according to the invention, having molecular weight 1220 g/mol and general formula I wherein R_1 is (III), R_2 is methyl, R_3 is ethyl, m=0; commercialised by Th. Goldschmidt AG (DE);

Polyether 2 = Tegomer® D-3123, ethoxylated and propoxylated diol according to the invention (EO/PO: 85/15), having molecular weight 1180 g/mol and general formula I wherein R_1 is (III), R_2 is methyl, R_3 is ethyl; commercialised by Th. Goldschmidt AG (DE);

Polyether 3 = polyether mono-alcohol obtained by ethoxylation of butanol, having molecular weight 1400 g/mol;

Polyether 4 = polyether mono-alcohol obtained by ethoxylation of butanol, having molecular weight 2000 g/mol;

Polyisocyanate 1 = Polurene® AD, reaction product of trimethylol propane and toluenediisocyanate (mixture of the isomers 2,4 and 2,6 in a ratio 80:20 by weight), having a NCO content of 13.0 ± 0,5% by weight, in ethyl acetate (with an active content of 75% by weight); commercialised by S.A.P.I.C.I. S.p.A. (Italy);

Polyisocyanate 2 = Tolonate® HDT LV2, product of isocyanuration of 1,6-diisocyanatohexane, with an NCO content of 23.0 ± 1% by weight (active content of 100% by weight); commercialised by Rhodia (France).

Example 1

A reaction vessel, equipped with internal thermometer, stirrer and cooler, is filled, under nitrogen atmosphere and at room temperature with 200.0 g (609.756 meq) of Polyisocyanate 1 and 43.4 g of N-methylpyrrolidone, then 67.0 g (109.756 meq) of Polyether 1 are added under stirring. The reaction temperature is brought to 60°C and maintained at 60°-65°C for about two hours, until the titrimetric determination of the free NCO-groups still present gives a value of 6.8% by weight (value determined in this example as well as in the other examples according to the standard method ASTM D2572).

The reaction mixture is diluted with 100.0 g of acetone and subsequently 52.2 g (600.000 meq) of butanone oxime are added dropwise over a period of about 1 hour, the reaction temperature not exceeding 70°C.

After 1 hour of reaction the prepolymer is checked to be NCO-negative according to the I.R. spectrum and, at about 60 °C, 564.3 g of demineralised water are added at a high stirring speed.

The organic solvents (ethyl acetate and acetone) are distilled off in vacuum.

A stable finely divided dispersion is obtained, with solids content of 30% by weight, pH 5.58, average particle diameters of 41.4 nm (determined by Coulter N4 Plus).

Percentage by weight of ethylene oxide groups related to the solids = 25%

IR (cm^{-1}): 3278, 2921, 1727, 1671, 1600, 1536, 1224, 1073, 997, 954, 893, 819, 766, 635, 471.

Example 2.

A reaction vessel, equipped with internal thermometer, stirrer and cooler, is filled, under nitrogen atmosphere and at room temperature with 200.0 g (609.756 meq) of Polyisocyanate 1 and 43.0 g of N-methylpyrrolidone, then 64.8 g (109,756 meq) of Polyether 2 are added under stirring.

The reaction temperature is brought to 60°C and maintained at 60°-65°C for about two hours, until the titrimetric determination of the free NCO-groups still present gives a value of 6.8% by weight.

The reaction mixture is then diluted with 100.0 g of acetone and subsequently 52.2 g (600.000 meq) of butanone oxime are added dropwise over a period of about 1 hour, the reaction temperature not exceeding 70°C.

After 1 hour of reaction the prepolymer is checked to be NCO-negative according to the I.R. spectrum and, at about 60 °C, 559.6 g of demineralised water are added at a high stirring speed.

The organic solvents (ethyl acetate and acetone) are distilled off in vacuum.

A stable milky dispersion is obtained, with solids content of 30% by weight, pH 4.86, average particle diameters of 59.7 nm (measured by Coulter N4 Plus).

Percentage by weight of ethylene oxide groups related to the solids = 21%

Example 3.

A reaction vessel, equipped with internal thermometer, stirrer and cooler, is filled, under nitrogen atmosphere and at room temperature with 200.0 g (609.756 meq) of Polyisocyanate 1 and 44.2 g of N-methylpyrrolidone, then 67.0 g (109.756 meq) of Polyether 1 are added under stirring.

The reaction temperature is brought to 60°C and maintained at 60°-65°C for about two hours, until the titrimetric determination of the free NCO-groups still present gives a value of 6.8% by weight.

The reaction mixture is then diluted with 100.0 g of acetone and subsequently 48.0 g (500.000 meq) of 3,5-dimethylpyrazole are added.

After 1 hour of reaction the prepolymer is checked to be NCO-negative according to the I.R. spectrum and 574.0 g of demineralised water are added at a high stirring speed.

The organic solvents (ethyl acetate and acetone) are distilled off in vacuum.

A stable milky dispersion is obtained, with solids content of 30%, pH 5.84, average particle diameters of 287.4 nm (measured by Coulter N4 Plus).

Percentage by weight of ethylene oxide groups related to the solids = 25%

IR (cm^{-1}): 3270, 2921, 1727, 1669, 1601, 1534, 1451, 1413, 1376, 1346, 1283, 1225, 1086, 1001, 968, 883, 817, 764, 744, 678, 658, 624, 508, 473, 457, 426.

Example 4 (Comparative).

A reaction vessel, equipped with internal thermometer, stirrer and cooler, is filled, under nitrogen atmosphere and at room temperature with 200.0 g (609.756 meq) of Polyisocyanate 1 and 57.9 g of N-methylpyrrolidone, then 153.7 g (109.756 meq) of Polyether 3 are added under stirring.

The reaction temperature is brought to 60°C and maintained at 60°-65°C. During the reaction the viscosity of the solution increases more and more, leading to gelification; the addition of 100.0 g of acetone reduces the viscosity only temporary, and the reaction is inevitably stopped.

Example 5.

A reaction vessel, equipped with internal thermometer, stirrer and cooler, is filled, under nitrogen atmosphere and at room temperature with 150.0 g (819.672 meq) of Polyisocyanate 2 and 49.7 g of N-methylpyrrolidone, then 90.0 g (147.541 meq) of Polyether 1 are added under stirring.

The reaction temperature is brought to 60°C and maintained at 60°-65°C for about two hours, until the titrimetric determination of the free NCO-groups still present gives a value of 9.8% by weight. Subsequently 64.3 g (739.344 meq) of butanone oxime are added dropwise over a period of about 1 hour, the reaction temperature not exceeding 70°C.

After 1 hour of reaction the prepolymer is checked to be NCO-negative according to the I.R. spectrum and the reaction mixture is dispersed in 640.9 g of demineralised water at a high stirring speed.

A dispersion is obtained with solids content of 30%, pH 5.58, average particle diameters of 275.9 nm (measured by Coulter N4 Plus).

Percentage by weight of ethylene oxide groups related to the solids = 30%

Example 6 (Comparative).

A reaction vessel, equipped with internal thermometer, stirrer and cooler, is filled, under nitrogen atmosphere and at room temperature with 75.0 g (409.836 meq) of Polyisocyanate 2 and 42.5 g of N-methylpyrrolidone, then 147.5 g (73.770 meq) of Polyether 4 are added under stirring.

The reaction temperature is brought to 60°C and mantained at 60°-65°C for about two hours, until the titrimetric determination of the free NCO-groups still present gives a value of 5.3% by weight.

Subsequently 32.3 g (336.066 meq) of 3,5-dimethylpyrazole are added slowly, the reaction temperature not exceeding 70°C.

After 1 hour of reaction the prepolymer is checked to be NCO-negative according to the I.R. spectrum and 552.1 g of demineralised water are added at a high stirring speed.

A coarse milky dispersion is obtained, with solids content of 30% and pH 6.19.

After 24 hours an evident sedimentation occurs and the average particle diameters can not be measured as it exceed s the upper limit of the instrument (3000 nm).

Percentage by weight of ethylene oxide groups related to the solids = 58%.

For easy of consultation the most significant parameters of the dispersions obtained in the Example 1-6 are resumed in the following Table (Table 1).

Table 1

EX.	POLYISOCYANATE	POLYETHER	R_{EQ} NCO/OH	BLOCKING AGENT	% NCO[1)]	DISPERSION STABILITY
1	Polyisocyanate 1	Polyether 1	10/1.8	MEKO[3)]	8.1	YES
2	Polyisocyanate 1	Polyether 2	10/1.8	MEKO[3)]	8.1	YES
3	Polyisocyanate 1	Polyether 1	10/1.8	3,5-DMP[4)]	7.9	YES
4	Polyisocyanate 1	Polyether 3	10/1.8	MEKO[3)]	6.1	NO
5	Polyisocyanate 2	Polyether 1	10/1.8	MEKO[3)]	9.5	YES
6	Polyisocyanate 2	Polyether 4	10/1.8	3,5-DMP[4)]	5.5	NO[2)]

1) Calculated as % of available isocyanate groups after de-blocking
2) after about 2 months the dispersion is completely separated
3) Butanone oxime
4) 3,5-dimethylpirazole

APPLICATION EXAMPLES

Textile finishing

Examples 7-9 resume the data obtained from the application tests conducted with the compositions for the oil- and water-repellent finishing of textiles, prepared with the dispersions described in the Examples 1, 2, 3, 5.

The oil- and water-repellent effect was determined using the test methods described below.

Water-repellency: the textile samples are evaluated according to AATCC-22 (Spray-test).

The water-repellency values are given according to the following scale:

100	No wetting, nor water drops on the surface
90	No wetting, but small water drops on the surface
80	Surface wetted on spray points
70	Surface partially wet
50	Surface totally wet
0	Wetting on the entire surface and back

Oil-repellency: the textile samples are evaluated according to AATCC-118.

The oil-repellency values are attributed according to the following scale, this test method being based on the resistance to wetting of the finished fabric by eight different liquid hydrocarbons of varying surface tension; the assessment scale in this test method covers grades from 1 to 8, grade 8 being the best (greatest repellent effect).

Oil repellency	Composition
1	Liquid paraffin (Kaydol)
2	65:35- Nujol : n-hexadecane
3	n-hexadecane
4	n-tetradecane
5	n-dodecane
6	n-decane
7	n-octane
8	n-heptane

Textile printing.

Example 10 reports the results obtained from the application tests conducted on textile samples printed with the printing pastes prepared using as cross-linkers the aqueous dispersions of the Examples 1, 2, 5.

The colour fastness of the prints was determined according to UNI 5153, that describes a method to establish the colour fastness of prints on fabrics of every nature when abraded and the consequent discharge of colour onto other fabrics.

The colour fastness was also determined according to UNI 7639, that describes a method to establish the colour fastness of a print on fabrics of different nature under the action of an artificial light source.

UNI 5153 describes a test where abrasion is produced by means of a dry fabric and another test where abrasion is produced by means of a wet fabric. An elevated value means a great colour fastness of the print according to both tests.

The values are from 1 to 5 according to UNI 5153 and from 1 to 8 according to UNI 7639. The washing fastness was also determined. The textile samples were washed 3 times at 40 °C (household washing), without intermediate drying and visually evaluated.

Example 7

Cotton fabrics are impregnated at Foulard with the following aqueous compositions for the oil- and water-repellent finishing of fabrics (Table 2, values expressed as g/l), squeezed in the padding mangle to an approximately 50% liquor pick-up, dried and baked at 150 °C for 1.5 minutes.

Table 2

	Comp. A	Comp. B	Comp. C	Comp. D	Comp. E
UNIDYNE®TG470[(1)]	27	27	27	27	27
MADEOL® NRW3[(2)]	1	1	1	1	1
Acetic acid (water sol. 10%)	1	1	1	1	1
Example 1		5			
Example 2			5		
Example 3				5	
Example 5					5

(1) fluorocarbon emulsion commercialised by DAIKIN INDUSTRIES LTD (JP)

(2) surfactant commercialised by Cesalpinia Chemicals SpA (Italy)

After 24 hours of conditioning at room temperature the fabrics are tested with the oil- and water-repellency tests.

The fabrics were also tested after repeated washing cycles.

Washes were performed at 40° C in a domestic washing machine, using a domestic detergent and dried in tumbler at about 80° C for 60 min after each washing cycle.

The test results are listed in the following table (Table 3).

Table 3

	Test method	No. of washes			
		0	1	3	5
Composition A	AATCC 22	100	90	70/80	0
	AATCC 118	4	4	2	2
Composition B	AATCC 22	100	100	100	100
	AATCC 118	4	6	4	3/4
Composition C	AATCC 22	100	100	100	100
	AATCC 118	4	6	3/4	4
Composition D	AATCC 22	100	100	100	100
	AATCC 118	4	6	3/4	3/4
Composition E	AATCC 22	100	100	90	70
	AATCC 118	3/4	4	3	2

Example 8

Polyamide fabrics are impregnated at Foulard with the following aqueous compositions for the oil- and water-repellent finishing of fabrics (Table 4, values expressed as g/l), squeezed in the padding mangle to an approximately 40% liquor pick-up, dried and baked at 150 °C for 1.5 min.

Table 4

	Comp. A	Comp. B	Comp. C	Comp. D	Comp. E
UNIDYNE®TG470[(1)]	27	27	27	27	27
MADEOL® NRW3[(2)]	1	1	1	1	1
Acetic acid (water solution10%)	1	1	1	1	1
Example 1		5			
Example 2			5		
Example 3				5	
Example 5					5

(1) fluorocarbon emulsion commercialised by DAIKIN INDUSTRIES LTD (JP)
(2) surfactant commercialised by Cesalpinia Chemicals SpA (Italy)

After 24 hours of conditioning at room temperature the fabrics are tested in the oil and water repellence tests.

The fabrics were also tested after repeated washing cycles. Washes were performed at 40 °C in a domestic washing machine, using a domestic detergent and dried in tumbler at about 80° C for 60 min. after each washing cycle. The test results are listed in the following table (Table 5).

Table 5

	Test method	No. of washes			
		0	1	3	5
Composition A	AATCC 22	100	100	100	100/90
	AATCC 118	3	2	1	0
Composition B	AATCC 22	100	100	100	100
	AATCC 118	3/4	2/3	1/2	1/2
Composition C	AATCC 22	100	100	100	100
	AATCC 118	3/4	2/3	1	0
Composition D	AATCC 22	100	100	100	100
	AATCC 118	3	1/2	1	1/2
Composition E	AATCC 22	100	100	100	100
	AATCC 118	2	1	1	1

Example 9

Polyester fabrics are impregnated at Foulard with the following aqueous compositions for the oil- and water-repellent finishing of fabrics (Table 6, values expressed as g/l), squeezed in the padding mangle to an approximately 30% liquor pick-up, dried and baked at 150 °C for 1.5 minutes.

Table 6

Composition	Comp. A	Comp. B	Comp. C	Comp. D	Comp. E
UNIDYNE®TG470[(1)]	27	27	27	27	27
MADEOL NRW3[(2)]	1	1	1	1	1
Acetic acid (water sol.10%)	1	1	1	1	1
Example 1		5			
Example 2			5		
Example 3				5	
Example 5					5

(1) fluorocarbon emulsion commercialised by DAIKIN INDUSTRIES LTD (JP)

(2) surfactant commercialised by Cesalpinia Chemicals SpA (Italy)

After 24 hours of conditioning at room temperature the fabrics are tested in the oil- and water-repellency tests. The fabrics were also tested after repeated washing cycles. Washes were performed at 40 °C in a domestic washing machine, using a domestic detergent and dried in tumbler at about 80° C for 60 min. after each washing cycle.

The test results are listed in the following table (Table 7).

Table 7

Finish	Test method	After washes			
		0	1	3	5
Composition A	AATCC 22	80	0	0	0
	AATCC 118	4	1	0	0
Composition B	AATCC 22	100	90	80	70
	AATCC 118	3/4	2	1/2	1
Composition C	AATCC 22	100	90/80	80	70/50
	AATCC 118	3/4	1	1	0
Composition D	AATCC 22	100	90/80	70	70/50
	AATCC 118	3	1	1	0
Composition E	AATCC 22	90	70	0	0
	AATCC 118	1	1	1	0

Example 10

The printing pastes (paste A, B, C and D) were prepared according to the compositions listed in Table 8.

The thus obtained printing pastes were used for silkscreen printing on four cotton fabrics.

Printing was performed onto the Zimmer magnetic table with a 55 wires/cm screen, by means of a 6 mm roller, at a rate of 50 (grades 10÷100), a pressure of 3 (grades 1÷6), in a single step.

After drying at 80°C, the prints were subsequently fixed at 160 °C for 3 min.

The colour fastness of the four cotton fabrics printed with the printing pastes A-D are listed in the following Table 9.

Table 8

g	Paste A	Paste B	Paste C	Paste D
water	782	782	782	782
DEFOMEX SI [1]	3	3	3	3
Ammonia 28 Bè	5	5	5	5
Binder Neoprint L 45[2]	150	150	150	150
Clear DP-GP[3]	20	20	20	20
Blue Neoprint LBS[4]	40	40	40	40
Lerisene VHF[5]	15			
Example 1		25		
Example 2			25	
Example 5				25

(1) Defoamer commercialised by Lamberti S.p.A (Italy)

(2) Ethyl-acrylate aqueous dispersion having an active content of 45% commercialised by Lamberti S.p.A. (Italy)

(3) Syntethic polyacrylate thickener partially neutralised with ammonia; commercialised by Lamberti S.p.A. (Italy)

(4) Water dispersion of an organic pigment (C.I. Pigment Blue 15:1); commercialised by Lamberti S.p.A. (Italy)

(5) Melamine resin with solids content of 50%; commercialised by Lamberti S.p.A. (Italy)

Table 9

	Test method	Evaluation	
Fabric printed with Paste A (comparative)	UNI 5153	Dry 1/2	Wet 4
	UNI 7639	>6*	
Fabric printed with Paste B	UNI 5153	Dry 3/4	Wet 3/4
	UNI 7639	>6*	
Fabric printed with Paste C	UNI 5153	Dry 3/4	Wet 4
	UNI 7639	>6*	
Fabric printed with Paste D	UNI 5153	Dry 4	Wet 4
	UNI 7639	>6*	

*After 141h of exposition the degradation of the fabric n° 6 of the blue scale begins, while the cotton fabrics printed with the Paste A-D do not show any visible degradation.

The cotton fabrics printed with the printing pastes prepared with the dispersions of this invention (Paste B, C and D) exhibit a washing fastness that is equal to that of the fabric printed with Paste A, which contains as cross-linker a standard melamine resin; they exhibit therefore a good washing fastness.